

In the process according to the invention strong protonic acids, in particular heteropoly acids, perchloric acid and perfluoroalkanesulfonic acids, can be used as initiator. Trifluoromethanesulfonic acid is the preferred initiator. The amount of the initiator generally is at least about 0.01 to about 1.0 ppm, based on the total amount of trioxane and comonomers. Preferably the amount of the initiator is from about 0.03 to about 0.4 ppm, and preferably from about 0.05 to about 0.2 ppm, based on the total amount of trioxane and comonomers.

Suitable formaldehyde dialkyl acetals used according to the invention are formaldehyde dimethyl acetal, formaldehyde diethyl acetal, formaldehyde dipropyl acetal, and formaldehyde dibutyl acetal. Formaldehyde dimethyl acetal, i.e. methylal, is preferred. The amount of formaldehyde dialkyl acetal, generally, is from about 3.4 to about 34 mmol per total kg of trioxane and comonomers.

Suitable comonomers of the present invention are generally known and may be selected from the group consisting of ethylene oxide, 1,3-dioxolane, 1,3-trioxepane, diethylene glycol formal, 1,4-butanediol formal, 1,3-dioxane, propylene oxide, trimethylene oxide, butadiene oxide, o-xylene glycol formal, thiodiglycol formal, 1,3-oxthiolane, and mixtures thereof. Particularly preferable comonomers are ethylene oxide, 1,3-dioxolane, diethylene glycol formal, and 1,4-butanediol formal. The amount of the comonomer utilized herein may range from about 0.2 to about 10% by weight, preferably from about 0.4 to about 5% by weight, based on the total amount of trioxane and comonomers.

The polymerization process according to the invention can be performed in any polymerization reactor or combination of reactors known for the production of POM polymers.

(10/90) mixture from which it was precipitated at room temperature. From the dried product the melt viscosity ratio (MVR) value and, through the measurement of the formaldehyde formation during 1 hour at 170° C. under alkaline conditions, the content of unstable terminal groups was determined (for data, cf. Table 1).

Examples 2 and 3

The procedure in Example 1 was utilized herein and additional amounts of methylal were added to the monomer mixture. The MVR and percent of unstabilized terminal groups are shown (for data, cf. Table 1).

Comparative Examples 4 through 6

Utilizing the procedure of Example 1, 96.6% by weight of trioxane was mixed with 3.4% by weight of dioxolane to form the monomer mixture. To this mixture 50 ppm of BF₃ gas and 0 ppm, 400 ppm or 1000 ppm of formaldehyde dimethyl acetal (Methylal) were added, respectively, to the monomer mixture of Examples 4, 5 and 6, the quantities in ppm being based on the total weight of the monomer mixture and being adjusted to obtain products having the same MVR values as in Examples 1-3, respectively. After an induction period of 30 seconds the polymerization started. The obtained crude polymer was quenched in a water/triethylamine mixture and subsequently hydrolyzed at 170° C. in a water/methanol (10/90) mixture from which it was precipitated at room temperature. The dried product was analyzed as in Examples 1-3.

TABLE 1

Example	Trioxane % b.w.	Dioxolane % b.w.	BF ₃ ppm	TFMSA in Methylal ppm/ppm	Additional Methylal ppm	Total Methylal ppm	MVR ml/10 cm	Unstable terminals %
1	96.6	3.4		0.2/500	0	500	2.5	0.04
2	96.6	3.4		0.2/500	500	1000	9	0.035
3	96.6	3.4		0.2/500	1000	1500	27	0.03
4	96.6	3.4	50		0	0	2.5	0.25
5	96.6	3.4	50		400	400	9	0.20
6	96.6	3.4	50		1000	1000	27	0.18

Further, antioxidants, acid acceptors, lubricants, waxes, UV stabilizers, nitrogen-containing co-stabilizers and other products known in the art for POM may be used as stabilizers and additives, either individually or in combination.

All fillers and reinforcing materials customary and known for plastics, in particular polyacetal copolymers, may be used as fillers and reinforcing materials.

EXAMPLES

Example 1

In a batch reactor operated at a temperature of about 80° C. and a pressure of about 1 atm., 96.6% by weight of trioxane was mixed with 3.4% by weight of dioxolane to form a monomer mixture. To this mixture 0.2 ppm of trifluoromethanesulfonic acid (TFMSA) dissolved in 500 ppm of formaldehyde dimethyl acetal (Methylal) were added, the quantities in ppm being based on the total weight of the monomer mixture. After an induction period of about 30 seconds the polymerization started. The obtained crude polymer was quenched in a water/triethylamine mixture and subsequently hydrolyzed at 170° C. in a water/methanol

In accordance with the data shown in Table 1, after the MVR values were adjusted in Examples 3, 4, and 5 to be equal to those of Examples 1, 2 and 3, the percentage of unstable terminal end groups of the polymers were dramatically reduced (see Examples 1, 2 and 3) wherein small amounts of trifluoromethanesulfonic acid dissolved in methylal were added to the reaction mixture.

We claim:

1. A process for the preparation of polyoxymethylene copolymers exhibiting a reduced amount of unstable terminal end groups comprising, polymerizing 1,3,5-trioxane with at least one cyclic ether and acetal comonomer with the aid of a strong protonic acid or Lewis acid initiator and in the presence of a formaldehyde dialkyl acetal, the improvement comprising dissolving the initiator in the formaldehyde dialkyl acetal before introducing the same to the trioxane and the comonomers.

2. The process according to claim 1, wherein the strong protonic acid initiator is selected from the group consisting of trifluoromethanesulfonic acid and anhydrides, pentafluoroethylsulfonic acid and anhydrides, heptafluoropropylsulfonic acid and anhydrides, nonafluorobutyl sulfonic acid and anhydrides, and perfluoroheptylsulfonic acid, anhydrides,

or

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and mixtures thereof and the Lewis acid is selected from the group consisting of phosphorus pentafluoride, silicon tetrafluoride, boron trifluoride, boron trifluoride etherates, tetrachloride, arsenic pentafluoride, triphenylmethyl hexafluorophosphate, and mixtures thereof.

3. The process according to claim 2, wherein the strong protonic acid initiator is trifluoromethanesulfonic acid and the Lewis acid is boron trifluoride.

4. The process according to claim 3, wherein the strong protonic acid or Lewis acid initiator is present in an amount of from about 0.01 to about 1 ppm, based on the total amount of trioxane and comonomers.

5. The process according to claim 4, wherein the formaldehyde dialkyl acetal is selected from the group consisting

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of formaldehyde dimethyl acetal, formaldehyde diethyl acetal, formaldehyde dipropyl acetal, formaldehyde dibutyl acetal, and mixtures thereof.

6. The process according to claim 5, wherein the formaldehyde dialkyl acetal is formaldehyde dimethyl acetal.

7. The process according to claim 6, wherein the formaldehyde dialkyl acetal is present in an amount of from about 3.4 to about 34 mmol per kg of trioxane and comonomers.

8. The process according to claim 2, wherein the formaldehyde dialkyl acetal containing the dissolved strong protonic acid initiator is added to the comonomers before admixing to the trioxane.

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